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RESEARCH ON MECHANISMS OF ALLOY STRENGTHENING

I. Strengthening Through Fine Particle Dispersion

II. Control of Structure and Properties by Means of Rapid Quenching of Liquid Metals (Splat Cooling)

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INTRODUCTION

The following is a six-month summary report of the individual research programs under the subject Grant. The items are discussed relatively briefly, with two main purposes in mind:

a) A delineation of the subject matter of the program,

b) An estimate of the progress made to date and any pertinent conclusions or observations warranted by the data.

In line with NASA recommendations, detailed information will come about primarily through publication of results in recognized journals, with appropriate copies mailed to NASA Headquarters.

I. DISPERSED PHASE ALLOYS

1. Surface oxidation plus internal oxidation

Following the success with the Cu-Al alloys, utilizing surface plus internal oxidation, three nickel-base alloys have been prepared and extruded. These are solid solution strengthened nickel-base alloys containing aluminum from 1 to about 6 weight percent. Part of the aluminum is converted to Al_2O_3, leaving increasing amounts in solution for additional strengthening and oxidation resistance. If as much as 3 percent aluminum remains unoxidized, it is likely that some gamma prime (Ni_3Al) will be precipitated.

The compositions of the starting -100 mesh argon atomized powders are given below.

	Compositions, in Weight Percent			
Alloy	Co	Mo	Al	Ni
Ni-1	20	7	1	bal
Ni-2	20	7	3	bal
Ni-3	20	7	6	bal

These powders were attrited to flakes less than one micron thick by 5 to 10 microns diameter. Five-pound batches were prepared and hydrogen reduced in a two-step sequence aimed at avoiding formation of the $NiO \cdot Al_2O_3$ spinel. X-ray identification of the extracted oxide showed 100% α- Al_2O_3, the stable high temperature form.

Extrusion was at 1800°F at an extrusion ratio of 16 to 1. The final as-extruded compositions are:

Extruded Alloy Compositions - Weight Percent

Alloy	Co	Mo	Al	Al_2O_3	Ni
Ni-1	19.8	6.9	-	1.88	bal
Ni-2	19.6	6.8	0.33	5.22	bal
Ni-3	19.2	6.7	1.42	8.54	bal

Except for Ni-1 these Al_2O_3 contents are much higher than desired if additional cold deformation after extrusion is desired. Further, too little aluminum remains in solution for effective solid solution strengthening and oxidation resistance.

Tension properties at 20°C are listed below.

As Extruded, Room Temperature Tension Properties

Alloy	0.2% Y. S. Ksi	U. T. S. Ksi	Elong. %	R. A. %
Ni-1	104	115	5.0	23.0
Ni-2	135	138	2.0	6.8
Ni-3	142	142	nil	2.0

These are very fine-grained alloys (near one micron) with some oxide stringering evident. Transmission EM studies showed both oxide segregation and an uneven dislocation distribution. The average particle sizes of the Al_2O_3 for the three alloys is:

Ni-1 270 Å
Ni-2 240 Å
Ni-3 220 Å

Stress rupture tests at 1800 and 2000°F for as-extruded material show:

Stress for 100 and 1000 Hour Life at 1800 and 2000°F for the As-Extruded Alloys

Alloy	Test Temp. °F	100 hr., Ksi	1000 hr., Ksi
Ni-1	1800	4.1	3.5
Ni-2	1800	3.8	2.2
Ni-3	1800	5.8	4.2
Ni-1	2000	2.0	in test
Ni-2	2000	2.8	in test
Ni-3	2000	2.5	in test

These are acceptable values for an extrusion ratio of 16 to 1; however, additional cold work is necessary to increase the strength levels. Cold swaging plus annealing treatments were, unfortunately, relatively unsuccessful because of the high volume content of Al_2O_3. Accordingly hot rolling was employed, and all alloys were reduced 80% at 1500°F. Alloy Ni-3 was fairly extensively cracked but Ni-1 and 2 produced useful test material. Tests are in process.

Al_2O_3 (α) is not as stable a refractory oxide as ThO_2; accordingly tests were run to determine the rate of coarsening of the Al_2O_3. The results are shown below for tests at 1250°C on alloy Ni-1.

Annealing time, hour	As-Ext.	1	10	50	100
Average size, Al_2O_3, Å	270	325	390	480	480

It became apparent during alloy processing that the Al_2O_3 content was significantly higher than desired. Accordingly three new alloys were processed wherein the oxide content was limited to about 2 volume percent, through control of the surface area of the attrited flake powders. The Al and Al_2O_3 contents of these new alloys (same base composition), after processing, are:

	w/o Al	v/o Al_2O_3
Ni-12	0.8	1.0
Ni-22	2.7	2.1
Ni-32	5.8	2.0

The alloys have been prepared in three pound batches and extruded at two different sets of conditions to achieve higher levels of stored energy; they are:

Reduction ratio of 20:1 at 1800°F
Reduction ratio of 30:1 at 2000°F

All alloys (6 total: 3 alloys and 2 extrusion conditions) were successfully hot extruded.

2. Ni-BeO Alloys: Surface Oxidized and Internally Oxidized

This program, involving both a pure Ni-base as well as complex alloys, originally utilized only internal oxidation of fine powders. Subsequently surface oxidation (only) of very fine powders was added. The eight alloys produced to date are listed in Table I below. Table II lists the extrusion variables for these same alloys.

The average oxide particle size is between 150 to 350 Å for these alloys. Alloys 1 to 4 showed BeO and $BeCr_2O_4$. Alloys 5 to 8 showed BeO essentially with traces of other oxides and compounds.

These alloys, after annealing, showed recrystallization to take place between 2000 and 2400°F; nevertheless, alloys 2 and 4 showed only a slight drop in hardness after one hour at 2400°F, and alloys 5 and 7 showed a slight decrease in hardness after annealing at 2200°F.

Room temperature tension tests on the as-extruded alloys are shown in Table III. Ductility values for all alloys are exceptionally high and clearly indicate a potential for considerable additional cold work for further strengthening. Alloy 7 shows the highest strength values (it also had the second highest hardness values after extrusion).

Stress rupture tests have been completed largely at 1800°F; the results are shown in Table IV. This table clearly shows that the internally oxidized alloys on average show higher stress rupture properties than do the surface oxidized alloys, as would be expected from the more homogeneous dispersion of BeO in the former case. Nevertheless the comparisons, after further cold work, are of great interest because of the much easier and cheaper processing method offered by simple surface oxidation.

TD-Ni is generally cold worked at least 90% after extrusion in order to achieve its reported stress rupture properties. Comparison of results from work with DS-Ni alloys and TD-Ni alloys also indicates a dependence on the particular thermomechanical treatments used.

In the present study cold work levels of 30, 60, and 70% R.A. were used with one hour annealing treatments after each 10% R.A. step. Table V shows typical improvements in rupture life and creep resistance of alloy $N1BeOS_2$ (Alloy 2) at 1800°F. Both the total amount of cold work, the amount per step, and the intermediate annealing temperature are of importance. These are currently being studied intensively utilizing transmission electron microscopy to establish the dislocation density, subgrain patterns, etc.

One of the important, unassessed variables, namely texture, is also being studied in these alloys in an effort to establish its contribution to strength and ductility.

TABLE I

Alloy Designation with Chemistries

No.	Alloy Designation	Composition	Remarks
1	$N1BeOS_1$	Ni-1 v/o BeO*	Small amount Cr_2O_3 as impurity
2	$N1BeOS_2$	Ni-1 v/o BeO*	Cr_2O_3 reduced
3	$N2BeOS_1$	Ni-2 v/o BeO*	Small amount Cr_2O_3 as impurity
4	$N2BeOS_2$	Ni-2 v/o BeO*	Cr_2O_3 reduced
5	$NM2BeOS_1$	Ni-4.5 Mo-2 v/oBeO	Surface oxidized
6	$NM2BeOI_1$	Ni-4.5 Mo-2 v/oBeO	Internally oxidized
7	$NMC2BeOS_1$	Ni-4.5 Mo-30 Co-2 v/o BeO	Surface oxidized
8	$NMC2BeOI_1$	Ni-4.5 Mo -30 Co-2 v/o BeO	Internally oxidized

* Machined chips for starting material; alloys 5 to 8 prepared from atomized powders.
Note: All compositions except BeO are in w/o.

TABLE II

Alloy & No.	Initial Density Before Extrusion. % of Theo. Density	Extrusion Data: Extrusion Temperature °F	Extrusion Data: Extrusion Ratio	Maximum Force in Tons: Upset	Maximum Force in Tons: Running	Ram Speed in./min.	K Factor: Upset	K Factor: Running
$NiBeOS_1$-1	72.0	1800	20:1	460	420	140	21.2	19.4
$NiBeOS_2$-2	78.0	1800	20:1	475	450	150	21.9	20.7
$N2BeOS_1$-3	68.0	1800	20:1	500	480	140	23.	22.
$N2BeOS_2$-4	76.0	1850	15:1	400	375	250	15.	14.
$NM2BeOS_1$-5	71.5	1800	20:1	525	425	150	24.2	19.5
$NM2BeOI_1$-6	78.0	1800	20:1	475	425	150	21.9	19.5
$NMC2BeOS_1$-7	70.0	1800	20:1	540	530	100	24.8	24.2
$NMC2BeOI_1$-8	70.0	1800	20:1	540	530	100	24.8	24.4

Note: $$K = \frac{\text{Force}}{\text{Area} \times 2.3 \times \log(\text{Reduction Ratio})}$$

TABLE III

Room Temperature Tension Properties for As-Extruded Condition

No.	Alloy	0.2% Offset yield strength psi	U.T.S. psi	Elong. %	R.A. %
1	$N1BeOS_1$	70,000	82,500	20.0	51.0
2	$N1BeOS_2$	35,000	57,000	32.0	92.0
3	$N2BeOS_1$	66,500	81,000	18.0	43.7
4	$N2BeOS_2$	42,000	67,000	26.2	64.0
5	$NM2BeOS_1$	60,000	85,000	22.8	43.0
6	$NM2BeOI_1$	56,000	80,000	23.8	43.5
7	$NMC2BeOS_1$	94,000	105,000	15.0	14.4
8	$NMC2BeOI_1$	60,000	83,500	26.4	43.5

TABLE IV

Stress-Rupture Data in As-Extruded Condition

No.	Alloy	Test Temp. ^oF	Stress for 100 hour rupture life, psi
1	$N1BeOS_1$	1800	920.0
2	$N1BeOS_2$	1800	2,850.0
3	$N2BeOS_1$	1800	3,000.0
4	$N2BeOS_2$	1800	3,200.0
5	$NM2BeOS_1$	1800	1,480.0
6	$NM2BeOI_1$	1800	2,600.0
7	$NMC2BeOS_1$	1800	1,080.0
8	$NMC2BeOI_1$	1800	4,000.0
9	$NMC2BeOI_1$	2000	1,600.0

TABLE V

Effect of Thermo-Mechanical Treatment on Creep-Rupture Properties of $NiBeOS_2$ (Alloy No. 2)

Alloy Condition	Test Temp. °F	Stress for 100 hour rupture life	Minimum creep rate at 3100 psi stress in inches/minute
(A) As-extruded	1800	2,850	9×10^{-5}
(B) 70% C. W. no intermediate anneal (I. A.)	1800	3,000	2.5×10^{-6}
(C) 70% C.W. with 1 hour I.A.* at 1800°F	1800	3,500	7.5×10^{-7}
(D) 70% C.W. with 1 hour I.A.* at 1500°F	1800	5,500	7.6×10^{-8}
(E) Same as (D)	2000	3,300	-

* Intermediate anneal at the specified temperature is after each 10% R. A. by swaging at room temperature.

3) Titanium Carbide Dispersion Strengthened Nickel-Base Alloys

Because it is believed that a carbide dispersoid is bonded in a nickel matrix whereas an oxide is not, it is expected that strength levels will be favorably affected by carbide dispersions especially at the low and intermediate temperatures. Thus far these expectations have been fully supported; however, the extent of the increase in strength as a function of carbide particle size, shape, distribution and volume content, and the limitations due to temperature effects have not been fully established. These are exciting alloys and will merit much additional study.

The solid solution strengthened alloys in powder form have been used as -325 mesh material and in the attrited condition. Thus far only the chromium free alloy has been studied, permitting internal carburization of the titanium in solution as the means of achieving the carbide dispersion. Table I summarizes the three alloys produced thus far, of which Alloy 1 is an extrusion of the non-carburized matrix as a control or reference material. Processing of Alloys 4 and 5 are described, and thermomechanical treatments are listed.

Table II lists the room temperature tension properties; excellent combinations of strength and ductility are noted, for example Alloy A5A. Stress rupture tests, Table III, on Alloy A5 (4.6 v/o TiC) clearly show the improvement with thermomechanical treatment. Again one must be reminded that the particular thermomechanical treatment utilized thus far is not necessarily the optimum one. For Alloy A5 a stress of approximately 7,000 psi is shown at 1800°F for

100 hours life; this compares with 8,000 psi for the A4 alloy which was considerably higher in carbide content. We are optimistic that further alloy development and variations in thermomechanical treatments will raise these stress levels to values of commercial interest.

In process for future work are finer carbides, more refractory carbides, other blending techniques, other processing treatments.

TABLE I

Summary of Alloy Manufacturing Procedures

Alloy	Carbon Content	Preparation of Powders	Deox. in H_2	Extrusion Temp. ^{o}F	Extrusion Ratio	Comments
1	0	As rec'd	None	1750	16:1	Matrix control
4	0.59 w/o	Attrit 4 days in isopropyl alcohol 20:1 ball/charge	30 hrs.; 1500^{o}F 24 hrs.; 1700^{o}F	1950	13.7:1	0.8 w/o C added initially; oxygen content = 0.92 w/o
4A	(Same as Alloy 4)					Swaged, cold, 20%
5	0.53 w/o	Blended a thick slurry of matrix carbon and isopropyl alcohol	15 hrs; 450^{o}C	1700	16:1	Oxygen = 0.028 w/o
5A	0.53 w/o	(Same as Alloy 5)				2 cycles*
5B	0.53 w/o	(Same as Alloy 5)				3 cycles
5C	0.53 w/o	(Same as Alloy 5)				4 cycles

* 1 cycle = swage 15%, 1900^{o}F 10 minutes.

TABLE II

Room Temperature Tension Properties

Alloy	Y. S., psi	U. T. S., psi	R. A., %	Elong., %
A1	96,000	160,000	-	41
A4	97,500	125,000	11	12
A5	85,000	134,000	30	30
A5A	105,000	147,000	32	29
A5B	92,000	146,500	44	13
A5C	68,100	126,500	40.5	35

TABLE III

Stress Rupture Data on Alloy A5

Alloy Condition	No. Cycles*	Stress for 100 hour life at 1800^{o}F, psi
A5	None	4,200
A5A	2	5,200
A5B	3	6,800
A5C	4	6,800

* 1 cycle = swage 15%, 1900^{o}F 10 minutes

4. Internally Oxidized Fe-BeO Alloys

These are continuing studies with this system which is ideal for studies of the mechanism of strengthening.

Two iron-beryllium alloys (Fe-0.1 Be and Fe-0.45 Be, nominal compositions) were selected for study. Ten pounds of powder of each alloy were obtained, attritted to near micron size flake, and reduced in dry hydrogen to convert the beryllium to beryllia. There was enough iron oxide present to completely convert the beryllium to BeO.

Establishing the optimum processing treatments required considerable effort because the oxygen content of the powder increased from $<1\%$ before attrition to $\sim 5\%$ after attrition. Because of available excess oxygen, a small amount of compound based on the chromite structure and composition $[Fe(Cr\text{-}Al)_2O_4]$ formed as well as beryllia. A hydrogen anneal at $600^{\circ}C$ (for four hours) was used to reduce the oxygen level to the level desired for internal oxidation immediately prior to annealing the attritted flake at $850^{\circ}C$ (for 48 hours) to convert the beryllium to beryllia. This procedure produced beryllia particles of about 400 Å in diameter (estimated from X-ray line broadening) and reduced the X-ray intensity of the chromite-like compound to $\leq$ 10% that of the beryllia.

Planned work for the next six months includes extrusion production, thermomechanical processing, tension and stress-rupture testing.

II. STRENGTHENING THROUGH STRUCTURE CONTROL THROUGH RAPID QUENCHING OF THE MELT

1. Splat Cooled Aluminum Alloys

As previously reported, microstructure analysis and lattice parameter measurements of splat cooled 2024 aluminum flakes indicated that the coarser flakes had the finer dendrite arm spacing and greater solid solubility of the constituent elements than the finer equi-axed powders. Therefore, three flake sizes were chosen for extrusion to determine the effect of flake size (cooling rate) on the final structure and mechanical properties.

The following three flake sizes (-8,+14 mesh; -14,+35 mesh; and -35,+100 mesh) were extruded at $300^{\circ}C$ and at a reduction ratio of 20:1. The extruded rods were then swaged to 50% reduction-in-area, solutionized at $495^{\circ}C$ for 1 hour, water quenched, and aged at room temperature.

The swaging and solutionizing treatments refined the long, straight powder particle boundaries present in the as-extruded condition. The splat cooled 2024 bars were now in the T4 (solutionized and naturally aged) condition and had comparable grain sizes (0.1 mm) to commercial 2024-T4.

The significant improvement in the splat cooled alloys was the refinement of the inclusion size from 10 to 20 microns in commercial 2024-T4 to 1 to 2 microns in the splat product.

Tensile properties: the room temperature tensile properties of splat cooled and commercial 2024 alloys are given in the table below.

Room Temperature Tensile Properties for 2024-T4 Alloys

Material	Y.S., psi	U.T.S., psi	Elong.,%	R. A.,%
Commercial 2024-T4	40,2000	67,200	22	37
2024 splat: -35 +100 mesh	41,000	71,200	21	34
2020 splat: -14,+35 mesh	43,800	74,600	22	40
2024 splat: -8,+14 mesh	47,300	78,700	24	39

As expected, the yield and tensile strengths increased with increasing flake size. An increase of 17% in yield and tensile strength over commercial 2024-T4 was found for the coarse (-8,+14 mesh) splat material. Ductilities were essentially the same for all alloys.

Fatigue properties: Since crack initiation occurs at the large intermetallic inclusions ($>$ 10 microns) in commercial 2024, a significant improvement was expected in the fatigue properties of the splat cooled alloys with a 1 micron inclusion size.

Constant load fatigue results have confirmed that this is indeed the case. At 30,000 psi where crack initiation is the controlling mechanism, fatigue lives have been improved by a factor of 4. Fatigue strength at 10^6 cycles, moreover, has been increased from 28,000 psi in commercial 2024 to 30,000 psi in the (-14,+35 mesh) alloy and 31,500 psi in the (-8,+ 14 mesh) splat cooled alloy.

At the high stress levels crack propagation is the controlling mechanism. Little change in fatigue lives has been observed in the high stress region, indicating a small difference in crack propagation rates of the splat cooled and commercial 2024 alloys.

Present work is concerned with studying the fracture mechanism in the commercial and splat cooled alloys. Of primary interest is the role of the inclusions in crack initiation and propagation. The scanning electron microscope is being used to examine the fatigue fracture surfaces of the two materials. Also, polished sections containing fatigue cracks are being observed with both the optical and scanning electron microscopes.

Stress-rupture properties: A considerable improvement in the stress rupture properties of the splat cooled 2024 alloys has been observed at 300°F. The 100 hour rupture life for 2024 aluminum has been increased from 52,000 psi in commercial materials to 58,300 psi in the (-14,+35 mesh) alloy and 60,600 psi in the (-8,+14 mesh) powder. The extrapolated 1000 hour rupture lives are 40,000 psi, 57,000 psi, and 60,000 psi, respectively. This is a 42 to 50 percent increase in the stress required for a 1000 hour rupture life at 300°F. The flat slopes of the stress rupture lines for the 2024 splat cooled alloys indicate the excellent structural stability of these alloys at 300°F.

Aluminum - 7% Silicon alloy: A high purity Al-7 wt.% Si alloy was rapidly quenched against a rotating copper disc. Metallographic and X-ray results again established that the coarser flakes had the finer dendrite spacing and greater amount of silicon in solution. After sieving, the (-8,+35 mesh) fraction was extruded at 300°C and a reduction ratio of 20:1.

The microstructure of the extruded alloy consisted of an extremely fine distribution of sub-micron silicon particles. Also present were long, straight powder particle boundaries parallel to the extrusion direction and considerable porosity due to poor particle bonding during the extrusion.

The room temperature tensile properties of the splat cooled Al-7% Si alloy are compared with those of commercial casting alloys and an air atomized Al-7% Si alloy in the table below.

Room Temperature Tensile Properties for Al-Si Alloys

Alloy	Condition	Y. S., psi	U.T.S., psi	Elong., %	R. A., %
Alloy 43 (5% Si)	Sand cast	8,000	19,000	8	-
	Perm. mold	9,000	23,000	10	-
	Die cast	16,000	33,000	9	-
Al-7% Si	Air atomized, As-extruded	17,300	27,600	26	41
Al-7% Si	Splat cooled, As-extruded	26,200	32,500	8	16

Note the considerable improvement in strength with increasing cooling rate due to the finer distribution of silicon particles. The lower than hoped for ductility in the splat cooled alloy is caused in part by some porosity and brittle longitudinal powder particle boundaries on which the Si precipitates. Scanning electron micrographs revealed a very fibrous fracture. The air atomized alloy, however, had a very ductile fracture as a result of a coarser Si precipitate which is less preferentially located at powder particle boundaries.

Other combinations of processing are warranted to achieve both high strength and high ductility. Stress rupture tests are now being run on the splat cooled alloy. Coarsening studies will also be performed to determine the structural stability of this alloy at elevated temperatures.

These exciting results suggest a promising future for the splat cooling technique in alloy development and the necessity for continued research in this area.

2. Aging Studies of Supersaturated Solid Solutions of Splat Cooled Al-Cu and Al-Fe Alloys

Specimens of Al - 1/2 and Al - 1 at. % Fe were splat cooled by the "piston and anvil" technique (cooling rate approximately 10^5 °C/sec) so that their aging behavior could be compared with that of the same alloys prepared by the "gun" technique (cooling rate greater than 10^7 °C/sec). Although both alloys are easily completely supersaturated when quenched at the faster cooling rate, limited evidence of supersaturation could be found in the less rapidly quenched alloys.

A small component of the lattice parameter change found in splat cooled Al alloys is caused by the splat process itself. A 0.05% decrease in the lattice parameter of 99.999% Al was measured in splats prepared by the gun technique. When the splats were annealed, the lattice parameter returned to its equilibrium value. Splats of 99.999% Al made by the piston and anvil method showed no lattice parameter change.

Considerable residual strain was found in splats of Al-4% Cu which were mechanically deformed by grinding. The already broad X-ray lines were further broadened 16 2/3% for specimens ground only one minute and broadened 25% for specimens ground for 5 minutes. The effect of this residual strain on aging behavior will be studied simultaneously with the alloying effects.

3. Study of Rapidly Quenched "Non-Crystalline" Metallic Alloys

The controlled atmosphere splat cooling apparatus was modified to allow cooling from higher temperatures up to 1300°C. An even higher melting temperature capability (up to 1700°C) is presently being incorporated into the melting unit. In addition, modifications are being made which will allow for multiple splats, with a goal of up to 8 splats in each run, to avoid the otherwise frequent opening and closing of the unit with long delay times. Non-crystalline metallic alloys are being investigated by electron microscopy, calorimetry and resistivity measurements in an effort to differentiate between amorphous and microcrystalline states. The alloy system of current interest is the Cu-Zr system.